

STATEMENT OF WORK

TITLE: Inject Micron-size Iron into Deteriorating Portions of the ISRM Barrier

KEY PROJECT TEAM MEMBERS

Project Manager (CAM): Scott Petersen
Technology Lead: Scott Petersen
DOE-RL: Mike Thompson
Project Engineer: Ron Clements
Safety and Health: Andy Foster
Project Control: Bonnie Howard
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1.0 BACKGROUND INFORMATION

Beginning in 1999, the In Situ Redox Manipulation (ISRM) barrier was installed to remediate a chromium groundwater plume in Hanford's 100-D Area. Using a network of 65 wells to access the groundwater, the ISRM technology was used to create a reducing zone in the aquifer by injecting sodium dithionite. This chemical reduced the native ferric iron (Fe^{3+}), which is naturally present in the aquifer sediments, to ferrous iron (Fe^{2+}). When groundwater contaminated with hexavalent chromium flows through the ISRM barrier it is converted to trivalent chromium (Cr^{3+}) by the reoxidation of Fe^{2+} . Trivalent chromium is virtually immobile in water and much less toxic than Cr^{6+} .

Laboratory experiments performed before installation of the ISRM barrier indicated that it would be effective for approximately 20 years, but localized signs of failure were discovered after only 18 months. Some of these wells were reinjected with sodium dithionite in 2002 to maintain the effectiveness of the barrier, but several of these began to show signs of failure again in less than two years. Approximately 20 wells within the barrier have lost a significant amount of reductive capacity only a few years after installation.

This barrier failure was the subject of two recent Technical Assistance Workshops (DOE 2004a,b). The cause of premature barrier breakdown was determined to be heterogeneities in the aquifer, where laterally discontinuous units with high permeability and lower inherent reductive capacity (because of lower iron content) were reoxidized faster than the less transmissive layers. In this conceptual model, the barrier wells would have to be reinjected periodically to reestablish the reducing environment in these more permeable layers. The Technical Assistance Panel recommended that an alternative technology be tested and possibly deployed to mend the barrier, to avoid periodically reinjecting the ISRM wells.

2.0 WORK DESCRIPTION

This work will test a new method to mend the In Situ Redox Manipulation (ISRM) barrier by injecting iron into the formation to supplement reduction capacity. This is one part of a larger “systems approach” designed to reduce chromium contamination reaching the Columbia River in the 100-D Area. This technology will both reestablish effectiveness and increase the longevity of the mended portions of the barrier. After some limited laboratory testing, the technology will be deployed in up to three ISRM boreholes.

Micron-size zero-valent iron (MZVI) will be injected into the most permeable zones of the ISRM barrier, together with a shear-thinning fluid containing polymer. Polymers are advantageous because they create a suspension that is viscous enough to keep the iron in solution for extended time periods to improve colloid movement into the porous media, but they do not cause a detrimental decrease in conductivity. The polymer will wash out of the aquifer by displacement and dilution through natural groundwater flow.

Laboratory tests have been performed to show that a slurry of MZVI and polymer can be injected into sediments and remain in suspension for a distance of over 1 m. At this distance MZVI concentrations are approximately 0.6 wt%; a 1-m wide barrier with this concentration would have an estimated longevity of over 7 years under the current chemical conditions. The goal of this test is to emplace MZVI into the formation at least 7 m from the injection well, which would result in overlapping treated zones between the ISRM wells, which are 12 m apart.

This Statement of Work includes a further discussion of the technology, a list of tasks to be performed, and the anticipated schedule and cost for all activities necessary to test this technology at the ISRM barrier. Appendix A contains responses to comments and suggestions made by the DOE Peer Review Committee regarding this work.

3.0 TECHNOLOGY DESCRIPTION

Permeable reactive barriers (PRB) containing zero-valent iron (ZVI) have been successfully used to remediate groundwater contamination for nearly 10 years. In the United States, there have been more than 90 applications of iron-based PRBs, 67 of which are full scale (ITRC, 2005). Nearly all of these have used the “trench and fill” method to emplace iron in the aquifer, which can only be economically constructed in areas with shallow groundwater. A few PRBs have recently been installed into deeper aquifers by injecting iron directly into them, either by vertical fracturing or hydraulic or pneumatic injection.

The injection of a PRB using a slurry containing MZVI and shear-thinning polymer is a unique application that has never been tested outside of the laboratory. This technology is ideally suited to mending the ISRM barrier because the slurry can be injected into the preferential pathways that exist in the 100-D aquifer. These pathways, the result of natural physical heterogeneity within the aquifer (DOE 2004), are the most likely cause of premature barrier breakdown because groundwater flowing through the pathways likely flushes large quantities of oxic water rapidly through the treatment zone, reducing its reductive capacity and longevity of barrier. Emplacing ZVI directly into these pathways will significantly augment the reductive capacity of

the ISRM barrier and increase its longevity. This technology is patented by Battelle Memorial Institute in Richland, Washington (Patent Number 5,857,810). The U. S. Government has the right to use this patent without royalty payments.

3.1 EXPERIMENTAL BASIS FOR TECHNOLOGY APPLICATION

In 2005, Fluor Hanford funded the Pacific Northwest National Laboratory to investigate the practicality of injecting a MZVI-polymer slurry into the 100-D aquifer, using intermediate scale laboratory tests (Oostrom et al., 2005). This work built on previous studies by Kaplan et al. (1996) and Cantrell et al. (1997a, b). In the first series of experiments, two different types of iron and two different types and concentrations of polymer were injected into 20-cm and 10-m long columns containing 12/20 Accusand to determine the most effective types and concentrations of amendments to use in a follow-on intermediate-scale experiment. These column studies determined that the most effective solution for injection was a concentration of 1 wt.% ZVI with an average diameter of 2 μm (S-3700 Fe⁰ colloids from International Specialty Products, Wayne, NJ), combined with 0.02% of the polymer Slurry Pro CDP (K.B. Technology, Chattanooga, TN). The injection rate determined to be optimum was 0.02 cm/s at the outflow end of the flow cell. Experiments using larger ZVI particles ($43 \pm 5 \mu\text{m}$, ARS Technologies, New Brunswick, NJ) showed that this material settled to the bottom of the column shortly after introduction.

After the column experiments, tests were performed in a wedge-shaped flow cell packed with aquifer material from the 100-D area. The flow cell was 20 cm deep, with a total volume of 59 L (15.6 gal). The porous media were packed into the flow cell to create either a high-permeability channel surrounded by low-permeability materials (Experiment 1) or a layered system with a high-permeability zone between two low-permeability zones (Experiment 2). After 30 pore volumes of slurry were injected, 320 samples were systematically collected from each experiment and analyzed for iron. Results from Experiment 1 are shown in Figure 1.

3.2 ADDITIONAL LABORATORY TESTS

Results from these column and wedge tests demonstrate that MZVI can be communicated into porous sediment over one meter from the point of injection in the laboratory. These experiments were not designed to evaluate the geochemical effects ZVI might have on groundwater, so further testing is required. The most important data that need to be determined are:

- Estimate the physical and chemical behavior of polymer under simulated groundwater conditions. Specific tests include:
 - estimating how groundwater displaces the polymer
 - determining how the polymer degrades over time
 - evaluating byproducts of polymer breakdown, including the potential to produce gasses (e.g., hydrogen, methane) during biodegradation
- Evaluate changes in water chemistry when groundwater of similar composition to that at 100-D Area reacts with MZVI. Important data to collect include:
 - pH changes
 - influence of strongly reducing conditions on nitrate (e.g., does it reduce all the way to ammonia)

- Investigate the potential for passivation of iron, especially under high groundwater carbonate concentrations

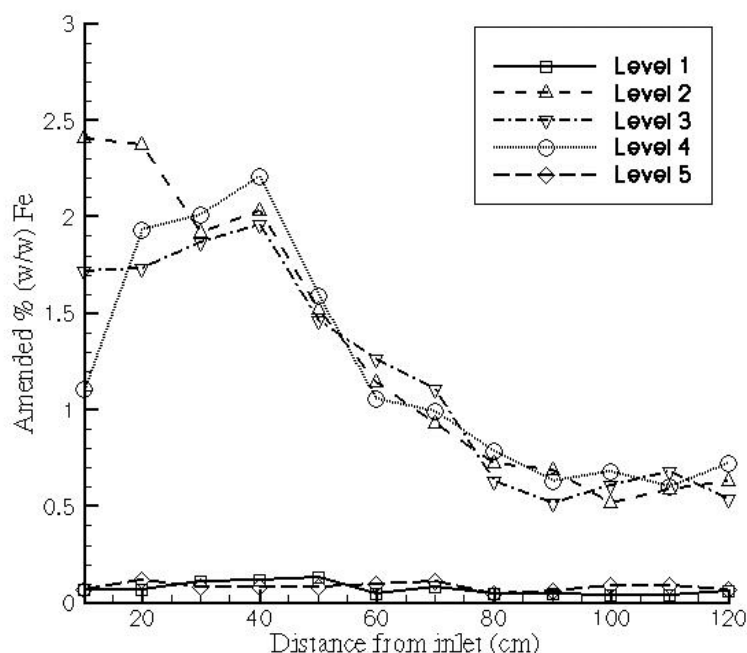


Figure 1. Amended Fe0 (wt %) at all Five Levels as a Function of Distance from Injection Location (Experiment 1)

4.0 DESCRIPTION OF WORK

The work described here is comprised of laboratory investigations, well drilling, design of iron emplacement procedures and equipment, iron slurry injection, verification testing, and groundwater monitoring. The laboratory test plan will be developed by the laboratory subcontractor prior to the start of testing. Work details for the field portion of the project will be developed in a work plan, which will include a treatability test plan and a sampling and analysis plan.

The treatability test plan will specify the objectives and approach for design and execution of the iron slurry injection. The design will detail the wells that will be injected, vertical intervals in the wells, slurry composition and requirements for handling (e.g., minimum temperature, safety considerations), and injection pressure. Injection details will include duration of injection at each well and interval, and monitoring of the injection and nearby wells to determine when to stop injecting. The test may be performed by injecting from a single well and/or circulating the slurry between two or more wells. Use of the latter technique should allow the slurry to communicate between two wells, thus forming a continuous barrier between injection wells. Flow modeling will be used to test various injection/extraction schemes in support of the treatability test plan.

There are several failing wells in the ISRM barrier that would be suitable for injection tests. Examples are 199-D4-9, 199-D4-26, and 199-D4-37. All three of these wells have monitoring wells in close proximity to them which could be used to gauge the progress of injection. An in situ conductivity meter would indicate when slurry began to influence the well, after which groundwater samples could be extracted for further analysis.

After completion of the injections a borehole will be drilled and samples collected from the aquifer formation near one of the injection wells. These will be analyzed for iron and other constituents, as determined in a Data Quality Objectives (DQO) process. A sampling and analysis plan, which will include results from the DQO, will be used to guide this sampling and groundwater monitoring after the injection.

4.1 TASKS TO BE PERFORMED

4.1.1 Task 1. Project Management

Tasks includes the labor for planning, management, supervision, attending safety meetings, responding to specific DOE-RL requests, interfacing with DOE-RL and the regulators, and oversight of all activities.

4.1.2 Task 2. Laboratory Testing

Procure and perform laboratory work necessary for detailed design and deployment of an iron injection system (Section 3.2). This will include testing for geochemical changes that may adversely affect groundwater after injection of MZVI.

4.1.3 Task 3. Work Plan

The Work Plan will detail the performance criteria for the technology, monitoring during the injection and post-injection phases, and characterization of the aquifer after injection. This Work Plan will include a treatability test plan and sampling and analysis plan, which will require regulatory approval.

4.1.4 Task 4. Acquire pre-injection characterization data from test wells to define aquifer properties

The main goal of this task is to determine vertical profiles of porosity in the aquifer. The electromagnetic borehole flowmeter will be used to obtain the data, possibly along with geophysical logging using neutron capture.

4.1.5 Task 5. Design and Construct the Injection System

Key tasks are formulation of the design criteria, specifications, drawings, a statement of work that will be used to solicit bids for the field work, supervision of construction and acceptance of the injection system.

4.1.6 Task 6. Field Testing

In this task, MZVI will be injected into selected boreholes, following the strategy outlined in the test plan (Task 3). Current plans are to contract this work, with site supervision.

4.1.7 Task 7. Monitoring

During injection, adjacent boreholes will be used to monitor the progress of injection and to evaluate the effectiveness of emplacing MZVI. After injection, several wells will be used to monitor for geochemical changes in the groundwater. This task includes the labor and analytical charges for both these monitoring efforts.

4.1.8 Task 8. Characterization Sampling

In this task one borehole will be drilled to evaluate the amount and distribution of MZVI deposited in the formation. Continuous cores will be collected, and samples from 6-in intervals will be collected and analyzed in the laboratory for iron. This task includes the labor for planning, drilling, and sampling one borehole along with the contracting price, and analytical charges.

4.1.9 Task 9. Evaluation report

This task includes the labor costs to prepare the evaluation report. The contents of the report will meet the overall requirements of a treatability test report as described in EPA guidance document EPA/540/R-92/071a.

4.2 MAJOR DELIVERABLES

Deliverable	Date
Transmit Work Plan Decisional Draft to RL	November 1, 2006
Initiate Field Test for Iron Injection	January 8, 2007
Transmit Decisional Draft to RL	September 28, 2007

4.3 BASIS AND ASSUMPTIONS FOR ESTIMATE

The following were used as guidance to formulate costs and schedules for this project. The schedule is presented in Figure 2. A summary of the budget is in Table 1.

- The project assumes that the authorization to proceed will occur by May 15, 2006.
- The scope of the estimate is to test the injection of MZVI at the ISRM barrier. Approximately three wells will be injected with an iron/polymer solution after laboratory tests have evaluated the potential of the technology to produce byproducts that may be detrimental to the aquifer. Monitoring will be performed during the injection test and afterward.
- Performance of the laboratory and injection work will be by contractor(s).
- Lab tests will confirm that pH will not significantly increase downgradient of the barrier
- Lab tests will confirm that significant amounts of ammonia will not be generated during treatment
- At least two boreholes will be injected with iron/polymer solution
- Injections will be performed in existing wells in or near the ISRM barrier

- Injections will occur at a period of high groundwater level, typically in January and June-July. If the work occurs in January, which is called for in the current schedule, contingencies must be built in for delays caused by inclement weather conditions.
- A borehole will be drilled to evaluate iron concentration in the aquifer material, so continuous core will be collected and analyzed
- Cost of the well drilling is based on FY 2005 actuals
- Project Management task includes informal weekly status reports to RL, semiannual reviews by DOE-HQ
- Final (reviewed) report will be completed un FY08, funded by Technology Management

The following process was used for developing the preliminary cost estimates for this project:

- The estimate process began by identifying the steps required to perform the work described for this project.
- Assumptions were identified and activities were detailed into manageable tasks. Meetings were then conducted with management and engineering to validate tasks and assumptions
- The activities were resource loaded with the anticipated resources to accomplish the work. Labor was estimated by the Cost Account Manager and engineering personnel based on previous injection operations. Material costs were based on discussions with potential vendors.
- Estimate excludes planning of resource overtime
- Assumes that the amount of waste to be managed will be negligible

Project Budget: \$900K

5.0 REFERENCES

- Cantrell KJ, DI Kaplan, and TJ Gilmore, 1997a, Injection of colloidal size particles of Fe⁰ in porous media with shear thinning fluids as a method to emplace a permeable reactive zone: *Land Contamination and Reclamation*, 5:253-257.
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- Kaplan DI, KJ Cantrell, TW Wietsma, and MA Potter, 1996, Retention of zero-valent iron colloids by sand columns: Application to chemical barrier formation: *J. of Environmental Quality*, 25:1086-1094.

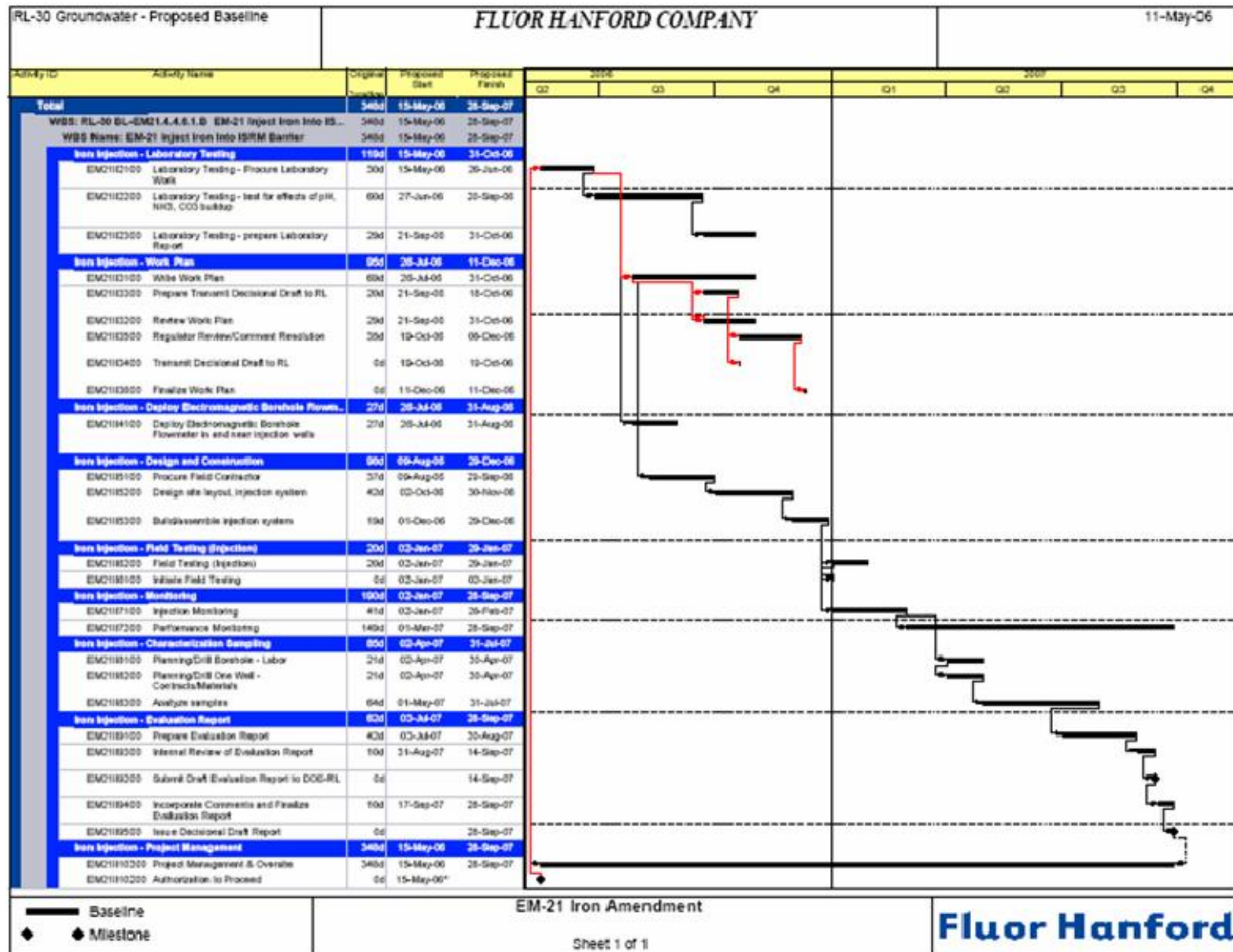


Figure 2. Schedule for ISRM Iron Injection Project

Responses to Supplemental Columbia River Protection Activities Peer Review

Proposal Title: Inject Micron-sized Iron into the Deteriorating Portions of the ISRM Barrier

Technical Basis of the Proposal:

The panel generally supports amending the existing ISRM barrier by injecting micron-sized ZVI in an aqueous polymer carrier within targeted intervals where breakthrough has occurred. However, the panel recognizes key issues, identified below, that remain to be addressed before implementation.

The panel believes the project is based on valid and appropriate science; ZVI is a potent reductant providing additional reducing capacity to mend the current ISRM barrier within targeted intervals that have been reoxidized. The concept of delivery within an aqueous polymer is novel. The concept is viable. The fact that this is part of a systems approach for the 100-D Area and that it builds upon the existing ISRM was well supported by the panel.

General technical issues are described below.

Delivery of the ZVI to appropriate locations within the aquifer remains a key uncertainty in assessing its performance. This uncertainty is impacted by the heterogeneity of the aquifer. Delivery of the ZVI is subject to the same vagaries of subsurface flow as was the dithionite.

- Potential settling of the ZVI at the base of high-conductivity intervals where injection occurs may significantly impact performance. Some method for monitoring needs to be developed.
 - **Response:** Agree
- Performance monitoring of ZVI delivery needs to be better developed. Consider drilling of monitoring points at various distances from the point of injection. Consider use of additional technologies such as borehole geophysics and cross-borehole geophysical tomography to monitor delivery.
 - **Response:** Agree. At least one test well will be located in an area with closely spaced wells that will be used for monitoring. We plan on drilling one additional well, and using geophysics to monitor the progress of injections.
- Consider delivery of a range of ZVI particle sizes to better mimic the natural porosity within the aquifer and potentially save money because the specifications for sizing will be less stringent.
 - **Response:** Agree. This will be considered
- Introduce the ZVI into the aquifer during the low river stage.
 - **Response:** Disagree. The upper portion of the aquifer is generally the most permeable and therefore most likely to oxidize rapidly to create the present situation. Therefore, the solution needs to be introduced during high river stage to adequately distribute the iron in this region.
- Introduction of a large number of pore volumes of fluid during injection could cause the spread of Cr-contaminated water and could impact the performance monitoring scheme significantly. Early monitoring results could easily be skewed by this effect.
 - **Response:** Comment noted

The presence of “co-contaminants” that are also reduced by ZVI and the generation of byproducts must be considered and monitored. Consider all geochemical impacts.

- **Response: Agree.** This will all be considered in the test plan.
- Assess the potential for ZVI to convert nitrate to ammonia, which could impact a variety of ecological receptors. A program for monitoring nitrate must be developed.
 - **Response: Agree.** Laboratory studies will be performed to evaluate the potential for producing ammonia from nitrate.
- Assess the potential for generation of high pH, which could impact downgradient water quality and possibly mobilize other metals. ZVI possesses a high pH between 10 and 14. Consider addition of pyrite to the ZVI to maintain lower pH. Add pH to the monitoring program.
 - **Response: Agree.** Laboratory studies will be performed to evaluate the pH changes expected by injection of iron/polymer solution.
- ZVI may reduce Cr+3 to Cr+2, which is mobile and will maintain a downgradient Cr plume if monitored as total Cr. This will mainly be a stakeholder perception issue, as the Cr+2 should reoxidize to Cr+3 some distance downgradient.
 - **Response: Comment noted.**
- Introduction of a guar gum polymer into the aquifer may provide a beneficial effect by supplementing the electron donors, but could also pose issues with hydrogen and methane gases that may be produced. The potential for generation of explosive hazard conditions should be examined.
 - **Response: Comment noted.** Hydrogen and methane will be monitored during the test.
- Consider elimination of the leaking Fire Retention Basin to reduce oxygen and groundwater flow to the ISRM. One recommendation is possible addition of solid particles of a reductant, such as ZVI or other iron materials.
 - **Response: Comment noted.** Discussions on basin decommissioning are continuing. Evaluate the longevity of the ZVI and don't overpromise its long-term performance.
- Interferences from ferric and ferrous iron coatings may reduce the longevity of the ZVI.
 - **Response: Comment noted.**
- High pH due to ZVI may cause precipitation of carbonates, which may reduce permeability and plug the barrier.
 - **Response: Comment noted.** This will be evaluated after the field test, and possibly in the laboratory as time allows.
- If calcium polysulfide is implemented upgradient, consider the introduction of sulfide and sulfate, which could passivate the ZVI surfaces.
 - **Response: Comment noted.**
- Include an improved description of the work content of the project. The proposal did not adequately describe the work to be conducted.

Response: Agree.

Other alternatives that could be considered include:

- Injecting iron (II)/iron (III) within the high-K zones of the barrier, if needed, and continuing with dithionite as a reducing agent.
- Better evaluation of the pump and treat system.

Implementation Strategy:

- The sequence and timing seem appropriate, although laboratory work should be directly focused on answering specific questions (e.g., byproducts, pH) and not just scaling up previous work. Further scaling is not needed. After some specific questions are answered by laboratory tests, the project should go to the field.
 - **Response:** Agree. The laboratory work will be significantly scaled back.
- The proposed budget costs appear to be high for some activities, especially the portion allocated for developing the test plan for lab work, which is not well described and should not focus on scaling. Costs for lab testing could likely be reduced and better spent in the field to enhance performance monitoring. There is not sufficient information to judge costs of implementation.
 - **Response:** Agree. Less emphasis will be placed on laboratory work and more on the field work and monitoring. The revised proposal will include more detail on schedule and budget.
- Perform field tests to determine the optimal amounts of polymer and ZVI, by injecting different amounts into different wells. Consider alternate injection/extraction schemes, to determine the appropriate amount of fluid to use during the injection to ensure delivery of the ZVI, but also limit the displacement of Cr-contaminated water during deployment.
 - **Response:** Agree. The field plan will include tests of different injection schemes and/or formulations.
- Clarify the location and philosophy of the ZVI injection.
 - **Response:** Agree. This will be further developed in the work plan. To summarize here, the areas that will be targeted for injection will be the two that have been exhibiting the majority of the breakdown: near D4-26 and D4-37. These two areas also have wells installed approximately 4 m up- and down-gradient; two of these wells are cased in PVC. More wells may be needed to adequately monitor the field test, but the current wells provide an excellent base on which to build the performance monitoring network.
- Consider using a dipole deployment to direct the barrier amendment and minimize the uncontrolled spread of groundwater during the deployment of pore volumes.
 - **Response:** This will be considered when formulating the work plan.
- Consider possible use of FLUTe system or redo of EBF in problem wells to identify target zones. This process was not explained in the proposal.
 - **Response:** Agree. EBF will be rerun in the testing areas.
- Implement a robust performance monitoring system. Establish specific objectives that can be measured.
 - **Response:** Agree that this is essential for evaluating the effectiveness of this technology and for refining design for future deployments.

Proposed Performance Metrics:

The panel generally agrees the proposed performance metrics are good but need more specifics.

- Outline performance measures so they clearly describe if goals/objectives are being met. Clarify the exit strategy (i.e., when to claim success). For example, specify concentrations of down-gradient parameters that will indicate success. Don't overpromise performance.
 - **Response:** Agree.
- Develop a robust monitoring program to measure near-term and long-term impacts.

- **Response:** Agree.
- Define a target for the lifetime of the treatment zone.
 - **Response:** Agree.
- Account for the relatively low Cr concentration during deployment, caused by the injected fluids displacing contaminated water up-gradient and down-gradient.
 - **Response:** Agree. This will be considered in the monitoring section of the work plan.
- Monitor for pH and associated byproducts in the groundwater and the river.
 - **Response:** Agree.
- Describe use of pump and treat system as a back-up/contingency treatment plan.
 - **Response:** Agree. The site is committed to continuing to passively treat the southwestern chromium plume in 100-D. If injection of micron-size iron doesn't turn out to be practicable, we would probably consider renewing the reductive capacity of the ISRM barrier by periodically injecting calcium polysulfide. Pump and treat may be considered at a later time, targeting the high-concentration center of the plume.
- Conduct monitoring frequently near the injection site, and install additional monitoring points away from injection sites to determine the radius of influence of the ZVI. Consider post-injection coring to monitor performance.
 - **Response:** Agree. Post-injection coring will yield essential data that will be used to make decisions on future deployment of this technology.